Molecular Switch

Thermal- and Photo-Induced Phase-Transition Behaviors of a Tapered Dendritic Liquid Crystal with Photochromic Azobenzene Mesogens and a Bicyclic Chiral Center

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Abstract: A ribbon-shaped chiral liquid crystalline (LC) dendrimer with photochromic azobenzene mesogens and an isosorbide chiral center (abbreviated as AZ_3DLC) was successfully synthesized and its major phase transitions were studied by using differential scanning calorimetry (DSC) and linear polarized optical microscopy (POM). Its ordered structures at different temperatures were further identified through structure-sensitive diffraction techniques. Based on the experimental results, it was found that the AZ_3DLC molecule exhibited the low-ordered chiral smectic (Sm*) LC phase with 6.31 nm periodicity at a high-temperature phase region. AZ_3DLC showed the reversible photoisomerization in both organic solvents and nematic (N) LC media. As a chiral-inducing agent, it exhibited a good solubility, a high helical-twisting power, and a large change in the helical-twisting power due to its photochemical isomerization in the commercially available N LC hosts. Therefore, we were able to reversibly "remote-control" the colors in the whole visible region by finely tuning the helical pitch of the spontaneously formed helical superstructures.

Introduction

Due to the unique structural properties and chemical multifunctionalities of dendritic molecules, dendrimers have been considered to be promising materials for advanced applications in nano- and biotechnologies. Meanwhile, liquid crystals (LC) with anisotropic properties and self-assembly abilities have been intensively studied and applied not only in electrooptical devices but also in molecular engineering nanotechnologies. Under these circumstances, the incorporation of LC to the dendritic system is helpful to control the hierarchical structures at different length scales, which can allow us to tune the physical properties of dendritic materials. Through sophisticated organic chemistry, intelligent dendritic LC molecules can be designed and tailor-made by modifying the chemical configurations as well as by adjusting the intermolecular physical interactions.

Additionally, if smart dendritic LCs responding the external stimuli can be prepared by connecting the photochromic and chiral moieties, we can apply those smart dendritic LCs in remote-controllable optical and biological materials and devices. The preparation of photochromic dendrimers exhibiting the formation of LC mesophases may present an evident scientific and practical interest because the low viscosity of the specifically designed dendrimers makes us to anticipate not only the high solubility into organic solvents or nematic (N) LC media but also the fast electro-optical response and rearrangement of their molecular structures under the external stimuli such as light and heat. It is also well-known that a chiral molecule can introduce the twisted molecular packing into an achiral N LC host to form a self-organized, optically tunable helical superstructure. When a chiral photochromic dendrimer is employed as a chiral dopant, it is possible to precisely control the pitch length of the helical superstructure by light, which paves the new way for the practical applications in optically addressable displays, optical data storages, and photonic crystals.

Here, we report the design and synthesis of a new ribbon-shaped chiral LC dendrimer containing photochromic azobenzene and an isosorbide chiral center. As described in Figure 1, the molecular structure of the tapered LC dendrimer (abbreviated as AZ_3DLC) is composed of two different groups: on the one hand, photochromic azobenzene derivatives can reversibly respond to lights, and on the other, the presence of a bicyclic diol group at the center may provide its molecular chirality.
and break the molecular packing symmetry. We also investigated thermal and photochemical behaviors of the photochromic chiral LC dendrimer in common organic solvents and in a typical N LC medium as well as in its mesophase.

Results and Discussion

As illustrated in Scheme 1, a ribbon-shaped chiral LC dendrimer (abbreviated as AZ3DLC, Figure 1) containing six photochromic azobenzene mesogens and a bicyclic chiral center is newly designed and synthesized. The detailed synthetic procedures are explained in the Experimental Section of this paper.

Chemical structures and purities of AZ3DLC and its intermediates are confirmed by $^1$H NMR spectroscopy (see Figures S1–S8 in the Supporting Information), thin-layer chromatography (TLC), $^{13}$C NMR spectroscopy (the Supporting Information, Figure S9), MALDI-TOF (Figure S10), and elemental analysis (Figure S11). The dendritic LC is specifically designed to enhance the nano-phase separation by locating the flexible hydrophobic alkyl tails and hydrophilic triethylene oxide (TEO) connectors to the methyl gallate at the both side of photochromic azobenzene mesogens. Since the photochromic azobenzene moiety is applied as the mesogenic group in AZ3DLC, the molecular conformations and phase structures of the ribbon-shaped chiral dendritic LC can be reversibly switched with respect to temperature and light. Here, the isosorbide chiral group is selectively chosen for the central core of AZ3DLC because the chiral compounds derived from bicyclic diols are very effective for breaking the molecular packing symmetries within the LC materials.

To determine the thermal transition temperatures and quantitative thermodynamic properties of the AZ3DLC compound, differential scanning calorimetry (DSC) experiments are conducted during cooling and subsequent heating at 10 °C min$^{-1}$, (Figure 1 and the Supporting Information, Figure S12). The thermal transition at 121 °C with $\Delta H = -52$ kJ mol$^{-1}$ is independent of the cooling rate, which is often observed from the isotropic (Iso) phase to a LC transition. On the other hand, the onset temperature and the heat of transition of the second exothermic transition exhibit the supercooling effect during a crystallization process. The lowest thermal transition below 77 °C could be originated from the reorganization of hydrophobic alkyl tails and TEO connectors. The thermodynamic properties obtained from the subsequent heating process are consistent with those from the cooling process. The formations of ordered phases are monitored under polarized optical microscopy (POM), as shown in Figure 2a. The photograph taken at 110 °C shows a fan-shaped tex-
tecture exhibiting a typical smectic LC phase. A further decrease in the temperature to 75 °C results in strong birefringent of focal conic defect aggregates, which is observed due to the anisotropic volume shrinkage during a crystallization process. The thermal transition below 70 °C does not change the POM image.

Based on the POM and DSC results, it is realized that there are two ordered phases below the $T_i = 121$ °C: one is a LC phase at high temperature region and the other is a crystalline phase at low temperature region. To investigate the temperature-dependent structural development of AZ3DLC, one-dimensional (1D) small angle X-ray scattering (SAXS) and wide angle X-ray diffraction (WAXD) patterns are obtained at different temperatures, as represented in Figure 2 b and c, respectively. Above 121 °C, AZ3DLC is in the Iso state, exhibiting only two amorphous halos at $2\theta = 2.15$ ($d = 4.11$ nm) and $19.1^{\circ}$ ($d = 0.46$ nm), which correspond to the average periodicity of electron density fluctuations among the nanophase-separated AZ3DLC and to the average distance between the amorphous mesogens, respectively.$^\text{[10]}$

Just below the $T_i = 121$ °C, three apparent low-angle reflections at $2\theta = 1.40$ ($d = 6.31$ nm), $2.81$ ($d = 3.15$ nm), and $4.22^\circ$ ($d = 2.10$ nm) start to develop. In addition to the changes of the low $2\theta$-angle region, a sudden narrowing of the high $2\theta$-angle-scattering halo occurs with a shift of the $2\theta$-angle from 19.1 to 20.2$^\circ$ ($d$-spacing from 0.46 to 0.44 nm). Based on the global equilibrium geometry of AZ3DLC calculated at 0 K utilizing the COMPASS force field of Cerius$^\text{®}$ 4.6 software, the theoretical length of AZ3DLC is 8.15 nm (the Supporting Information, Figure S13). Although the calculation is based on the all-trans conformation of alkyl, azobenzene, and TEO groups, the calculated length (8.15 nm) is significantly bigger than the detected layer spacing ($d = 6.31$ nm). Note that the lower $d$-spacings of AZ3DLC molecule indicative of either a tilted arrangement along the long axis of the smectic phase or interdigitation of the smectic layers.$^\text{[11]}$ However, the $q$-values of low angle diffractions are 1:2:3 and the broad scattering halo (liquid-like lateral short-range ordering within the layer) is detected in the high-angle region.$^\text{[12]}$ It is realized that AZ3DLC keeps the ribbon-shaped chiral dendritic conformation in the presence of a bicyclic diol center as a chiral group between the dendronized azobenzene moieties. From the experimental results and careful analysis, AZ3DLC should be a low-ordered chiral smectic (Sm*) LC phase between 77 and 121 °C.

At 75 °C, many sharp reflection peaks observed in the wide-angle region indicate that the high-ordered crystalline structure is formed in the layers. As shown in Figure 2 c, three diffractions ($2\theta = 1.40$, 2.81, and 4.22$^\circ$) observed in the Sm* phase shift to higher $2\theta$-angles at $2\theta = 1.51$, 3.02, and 4.55°. These diffraction shifts explain the fact that the anisotropic volume shrinkage during the crystallization process mainly occurs along the layer normal. The additional odd numbered diffractions at $2\theta = 3.78$ ($d = 2.34$ nm) and $5.24^\circ$ ($d = 1.67$ nm) at a low-angle region represent that the phase at the lower temperature could be an anticlinically tilted chiral smectic crystalline structure. Since the orientation of molecular packing structure between LC phase and highly ordered crystal phase does not significantly change during the phase transition, the most probable chain conformations and molecular packing in the LC phase must retain an anticlinically tilted chiral smectic phase between 77 and 121 °C.$^\text{[13]}$ However, more detailed LC and crystalline structures and the molecular packing of these azobenzene-based chiral molecules should be further investigated by using the 2D WAXD studies with aligned samples.

The photochemical behaviors of the AZ3DLC compound with six photochromic azobenzene groups are first investigated by ultraviolet/visible (UV/Vis) spectroscopy in a chloroform solution ($2 \times 10^{-2}$ nm) and the results are summarized in Figure 3. UV-light irradiation with a maximum intensity at 365 nm (Xenon arc lamp, 100 mW cm$^{-2}$), the thermodynamically stable trans conformer of azobenzene transforms to its metastable cis conformer and reaches into a new photostationary state in 160 s. As indicated in Figure 3 a, the absorption band between two isosbestic points (320 and 430 nm) resulting in the π- to π* transition is originated from the trans-form of azobenzene, whereas the ground state (n) of the cis conformer of azobenzene is excited to the π* state by absorbing the UV light in the range of 430–540 nm.

On the other hand, upon subsequently being exposed to Vis light (450 nm), the amount of trans conformational azobenzene isomer is increased by concomitantly decreasing the intensity and area of the absorption band for the trans/cis isomers of azobenzene. Transition between two photostationary equilibrium states is a fully reversible process by alternating UV- and Vis-light, which can allow us to fabricate a reversible photomodulating device.$^\text{[14]}$ As represented in Figure 3 c, it is worth mentioning the fact that not only the cycle is repeated, but also the amplitude of the change is remained without degradation.

The peculiar $\text{trans- cis}$ photoisomerization process of AZ3DLC compound is very useful and attractive for light-driven molecular switches because this phenomenon may be used to
modulate the LC phase by alternating UV and Vis light. To realize its potential in the practical applications for optical devices, however, an efficient trans$\rightarrow$cis photoisomerization process of the AZ DC compound is required even in its LC mesophase. Therefore, photoisomerization of AZ DLC in the bulk is investigated systematically. Upon UV-light irradiation of the Sm* phase, the population of the cis conformer is gradually increased and the long-range molecular orders disappear, which in consequence leads to the Sm* $\rightarrow$ Iso phase transitions within 30 s (Figure 4). When the irradiated UV-light is blocked, the Iso phase returns back to the Sm* phase. The corresponding photochemical switching process in AZ DLC can be schematically represented as shown at the top of Figure 4.

By doping the ribbon-shaped chiral dendritic AZ DLC molecule (16 wt.% into an achiral N LC host (E7), a chiral N LC phase (N*) is formed. As shown in Figure 5a, the typical cholesteric fingerprint texture is observed under a vertically aligned surface condition. The helical axis of the helical superstructure is perpendicular to the surface normal and the helical pitch is estimated to be 62 $\mu$m. When the LC mixture is irradiated with UV light at 365 nm, the helical pitch length of the N* phase is gradually increased and a typical Schlieren textures of the achiral N phase are observed in 5 s (Figure 5b). The N* $\rightarrow$ N phase transition is originated by the fact that the azobenzene cis conformers interrupt the continuous twisting molecular packing with neighboring E7 LC host molecules. Upon further irradiation of UV light, the dark spot starts to appear in the N phase (Figure 5c) and it develops quickly, and eventually the N $\rightarrow$ Iso phase transition takes place throughout the whole irradiated area (Figure 5d). By irradiating Vis light on the Iso phase for 30 s at room temperature, the helical superstructure with a fingerprint texture is reversibly constructed again. This result represents that it is possible to control the phase transitions by tuning the wavelength of irradiated light.

A planar alignment of helical LC superstructure can be achieved by introducing a planar alignment layer on the surface of LC cell sandwiched with antiparallel rubbing directions. When the N* LC mixture of 16 wt.% AZ DLC in E7 is capillary filled into the planar aligned LC cell with a 10 $\mu$m cell gap, a uniform reddish color is observed from the transmission mode POM throughout the whole LC cell (Figure 6). Since the helical axis of spontaneously formed helical superstructure is
parallel to the surface normal and constructs a 1D photonic crystal in which the refractive index changes periodically along the helix axis, the visible light with a specific wavelength can be selectively filtered or reflected by the opened photonic band gap. The photonic band gap can be tuned by controlling the helical pitch length of N* LC. Upon UV-light irradiation, the initial reddish (R) color is changed to green (G) in only about 16 s and further turned into a new photostationary state in 58 s with a blue (B) color. The new photostationary state can be reversibly switched back to the initial state (R) within 30 s and further turned into a new photostationary state in 58 s with a blue (B) color. The new photostationary state can be reversibly switched back to the initial state (R) within 30 s by irradiating with Vis light. The reversible tuning of polarized light across RGB colors was repeated many times without noticeable degradation.

Conclusion

The ribbon-shaped tapered chiral liquid crystalline (LC) dendrimer (abbreviated as AZ3DLC) containing both a chiral bicyclic unit and six photochromic azobenzene mesogens was newly designed and successfully synthesized. From the structure-sensitive diffraction experiments combined with thermal and morphological results, it was recognized that AZ3DLC formed two ordered phase structures: one is a low-ordered chiral smectic LC phase at high temperatures, and the other is an anti-parallel to the surface normal and constructs a 1D photonic crystal in which the refractive index changes periodically along the helix axis, the visible light with a specific wavelength can be selectively filtered or reflected by the opened photonic band gap. The photonic band gap can be tuned by controlling the helical pitch length of N* LC. Upon UV-light irradiation, the initial reddish (R) color is changed to green (G) in only about 16 s and further turned into a new photostationary state in 58 s with a blue (B) color. The new photostationary state can be reversibly switched back to the initial state (R) within 30 s by irradiating with Vis light. The reversible tuning of polarized light across RGB colors was repeated many times without noticeable degradation.

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Experimental Section

General

The thermal behavior was monitored by using a PerkinElmer PYRIS Diamond DSC equipped with an Intracooler 2P apparatus. The transition temperatures were determined by measuring the onset temperatures obtained during the cooling and heating scans. 1D WAXD experiments were conducted in the reflection mode of a Rigaku 12 kW rotating-anode X-ray (CuKα radiation) generator coupled with a diffractometer. The diffraction peak positions and widths were calibrated with silicon crystals. Samples were scanned across a 2θ-angle range of 1.5 to 35° at a scanning rate of 2° min⁻¹. 1D SAXS measurements are used to study the phase structure. The X-ray beam is produced by a CuKα microsource (Rigaku). The SAXS intensity profiles were plotted against q = 4πsinθ/λ, in which λ is the wavelength of X-ray (λ = 0.124 nm) and 2θ is the scattering angle. The change of optical textures at a given temperature was observed by using cross-polarized POM (Nikon ECLIPSE E600POL) coupled with a LINKAM LTS 350 heating stage. 1H NMR and 13C NMR spectra were recorded on a JNM-EX400 spectrometer in deuterated chloroform (CDCl3). Elemental analysis (Vario EL) and MALDI-TOF MS (Voyager-DE STR Biospectrometry Workstation) experiments were conducted to identify the chemical structure. UV/Vis absorption spectra were obtained with a SCINCO 5-3100 spectrometer. Additionally, the Cerius2 simulation software from Accelrys (Version 4.6) was also used to calculate the minimal-energy geometry in the isolated gas-phase utilizing the COMPASS force field.

Syntheses

1-Nitro-4-(octyloxy)benzene (1): A solution of 1-bromoocctane (8 g, 41.43 mmol), 4-nitrophenol (6.92 g, 49.72 mmol) and K2CO3 (6.87 g, 49.72 mmol) in anhydrous DMF (100 mL) was heated at reflux for 6 h. After the reaction, the solvent was removed in vacuum and the remaining residue was dissolved in chloroform (200 mL) and washed with distilled water several times. After drying the organic layer over MgSO4, it was purified by column chromatography with silica gel using CHCl3/n-hexane = 1:2. The resulting product was a pale-yellow viscous liquid (Yield: 77 %, 8.02 g).

1H NMR (400 MHz, CDCl3, TMS): δ = 0.89 (t, 3 H), 1.23–1.51 (m, 10 H), 1.80 (m, 2 H), 4.02 (t, 2 H), 6.93 (d, 2 H), 7.21 ppm (d, 2 H).

4-(Octyloxy)benzenamine (2): Hydrazine monohydrate (1.10 g) was added drop-wise to a solution of 1 (2.82 g) in EtOH (40 mL). After the solution was heated to 45°C, the activated Raney-nickel was added in portions until no further reaction was observed. The resulting mixture was filtered off, and the ethanol was removed under reduced pressure. The crude was dissolved in diethyl ether and washed with water and brine, and then dried with MgSO4. After distilling the solvent, the product was obtained as brownish oil which was used without further purification (Yield: 93 %, 2.31 g).

1H NMR (400 MHz, CDCl3, TMS): δ = 0.89 (t, 3 H), 1.23–1.51 (m, 10 H), 1.80 (m, 2 H), 3.2–3.7 (s, 2 H), 3.85 (t, 2 H), 6.63 (d, 2 H), 6.75 ppm (d, 2 H).

4-(4-Octyloxy)hydroxazoxybenzene (3): A 2.5 m NaOH solution (1.35 mL) was added slowly (drop-wise) at a temperature below 5°C to a heterogeneous mixture of 2 (7.2 g) in 5 m HCl (17.6 mL). The mixture was held at ≈5°C and added carefully to a solution of phenol (3.1 g) in 2 m NaOH (27 mL). The product was precipitated by the addition of small portion of NaCl. By the recrystallization of the product in hexanes, the purified reddish crystal was collected (Yield: 74 %, 7.83 g).

1H NMR (400 MHz, CDCl3, TMS): δ = 0.89 (t,
of 3 (4 g, 12.25 mmol), TEO (8.26 g, 49 mmol), and K$_2$CO$_3$ (6.77 g, 49 mmol) in dried DMF (100 mL) was heated at reflux for 24 h. After the reaction, the solvent was removed in vacuum and remaining residue was dissolved in ethyl acetate and extracted with distilled water several times. The organic layer was dried over MgSO$_4$. The purified product by recrystallization from CHCl$_3$ and EtOH was a waxy yellow solid (yield: 88 %, 4.11 g). $^1$H NMR (400 MHz, CDCl$_3$, TMS): $\delta$ = 0.89 (t, 3 H), 1.23–1.51 (m, 10 H), 1.80 (m, 2 H), 3.64 (t, 4 H), 3.74 (m, 4 H), 3.89 (t, 2 H), 4.02 (t, 2 H), 2.41 (t, 4 H), 6.99 (q, 4 H), 7.24 (s, 2 H), 7.31 (s, 2 H), 7.83 ppm (q, 24 H); $^{13}$C NMR (400 MHz, CDCl$_3$, TMS): $\delta$ = 161.2, 160.6, 152.4, 147.1, 146.8, 124.3, 124.2, 114.7, 109.2, 72.5, 70.8, 70.6, 69.6, 68.9, 68.3, 67.6, 31.7, 29.2, 26.0, 22.6, 14.11 ppm; MS (MALDI-TOF): m/z calcld: 3093.69 [M+K]+; found: 3131.66; elemental analysis calcld (%) for C$_{30}$H$_{23}$O$_{12}$N$_2$: C 68.9, H 6.3, N 20.8; found: C 68.7, H 7.329, N 5.371.

### Acknowledgements

This work was mainly supported by the Human Resource Training Project for Regional Innovation, Basic Science Research Program (2013R1A1A0207238), Converging Research Center Program (2013K001428) and BK21Plus Program, Korea. D.Y.K. appreciates the support from Global Ph.D Fellowship Program (2013H1A21033907) and K.U.J. acknowledges the support from LG Yonam Foundation.

### Keywords

chirality · dendrimers · liquid crystals · phase transitions · photochromism


Received: October 7, 2013
Revised: February 10, 2014
Published online on March 24, 2014